The physics of dynamical atomic charges : the case of ABO₃ compounds

Ph. Ghosez[†], J.-P. Michenaud and X. Gonze

Unité de Physico-Chimie et de Physique des Matériaux, Université Catholique de Louvain,
1 Place Croix du Sud, B-1348 Louvain-la-Neuve, Belgium

(February 1, 2008)

Based on recent first-principles computations in perovskite compounds, especially BaTiO₃, we examine the significance of the Born effective charge concept and contrast it with other atomic charge definitions, either static (Mulliken, Bader...) or dynamical (Callen, Szigeti...). It is shown that static and dynamical charges are not driven by the same underlying parameters. A unified treatment of dynamical charges in periodic solids and large clusters is proposed. The origin of the difference between static and dynamical charges is discussed in terms of local polarizability and delocalized transfers of charge : local models succeed in reproducing anomalous effective charges thanks to large atomic polarizabilities but, in ABO₃ compounds, ab initio calculations favor the physical picture based upon transfer of charges. Various results concerning barium and strontium titanates are presented. The origin of anomalous Born effective charges is discussed thanks to a band-by-band decomposition which allows to identify the displacement of the Wannier center of separated bands induced by an atomic displacement. The sensitivity of the Born effective charges to microscopic and macroscopic strains is examined. Finally, we estimate the spontaneous polarization in the four phases of barium titanate.

I. INTRODUCTION

For a long time, there has been a continuing interest in the definition of atomic charges in solid state physics as well as in chemistry [1–4]. This interest lies essentially in the fact that the concept of atomic charge naturally arises in a large diversity of frameworks and is frequently helpful for a simple description of solids and molecules. The variety of contexts in which the charge is involved (IR spectrum analysis, XPS chemical shifts analysis, theory of ionic conductivity of oxides, determination of electrostatic potential, definition of oxidation states...) underlines its central role but also reveals a concomitant problem: inspired by various models or by the description of various physical phenomena, many different definitions have been proposed that, unfortunately, are not equivalent [4].

Following a distinction already made by Cochran [1], it seems possible to classify the different concepts into static and dynamical charges. The *static* charge is an intuitive concept, usually based on a partitioning of the ground-state electronic density into contributions attributed to the different atoms. It is an ill-defined quantity that depends on the convention artificially chosen to affect a given electron to a particular ion [1,2]. On the other hand, the *dynamical* charge is directly related to the change of polarization (or dipole moment, for molecules) created by an atomic displacement. This change of polarization is a quantity that can be experimentally measured, at least in principles, giving the dynamical charge a well-defined character.

In order to clarify the concept of atomic charge, it was important to compare on practical examples the numerical results obtained from its different definitions. Recent studies of the statistical correlation between various atomic charges using a principal component analysis have suggested that the different definitions are not independent but correspond to different scales driven by a unique underlying physical factor [4]. If this assertion seems plausible as far as static charges are concerned, we will argue that the dynamical charge should not reduce to the same physical factor but should also depend on an additional parameter: the rate of transfer of charge, influenced by the bonding with the other atoms of the system and additionally, for large systems, by the condition imposed on the macroscopic electric field.

The Born effective charge tensor $Z^{*(T)}$ – alias transverse charge –, that is at the center of the present study, is a dynamical quantity introduced by Born [5] in 1933. In solid state physics, it is since a long time considered as a fundamental quantity because it monitors the long-range Coulomb interaction responsible of the splitting between transverse and longitudinal optic phonon modes [5]. During the seventies, the Born effective charges were already investigated and discussed within empirical approaches (see for example Harrison [6]). More recently, they became accessible to first-principles calculations [7–9], and accurate values have been reported for a large variety of materials.

For the case of ABO₃ compounds, old experimental data [10] and empirical studies [6] had suggested that the amplitude of the Born effective charges should deviate substantially from the amplitude of the static atomic charge. Surprisingly, this result remained in the dark until first-principles calculations confirmed that the components of $Z^{*(T)}$

are anomalously large in these oxides [11–13]. It was observed that the components of $Z^{*(T)}$ can reach twice that of the nominal ionic charges. This result reopened the discussion on the physics of the Born effective charges and different recent studies tried to clarify the microscopic processes monitoring the amplitude of $Z^{*(T)}$.

In this paper, we first clarify the relationship between various atomic charges. We then present results concerning $BaTiO_3$ and $SrTiO_3$ in order to illustrate how a careful analysis of the Born effective charges can teach us interesting physics concerning these compounds. It reveals the mixed ionic and covalent character of the bond [14,15]. It allows to visualize the mechanism of polarization as electronic currents produced by dynamical changes of orbital hybridizations [6,15]. It also clarifies the origin of the giant destabilizing dipole-dipole interaction producing the ferroelectric instability of these materials [16].

In Section II and III, we contrast the concepts of static and dynamical charges and we reintroduce the Born effective charge that is at the center of the present discussion. In Section IV, we compare various results obtained within different frameworks for the cubic phase of $BaTiO_3$ and $SrTiO_3$. The bond orbital model of Harrison is explicitly applied to $SrTiO_3$ (Appendix A). We also discuss the origin of the large anomalous contributions in terms of local electronic polarizability and dynamical changes of orbital hybridization. A decomposition of the role played by the different bands is reported in Section V. Section VI is devoted to the evolution of the Born effective charges in the three ferroelectric phases of $BaTiO_3$ as well as in the cubic phase under hydrostatic pressure. This points out the role of the anisotropy of the atomic environment on the amplitude of $Z^{*(T)}$. Finally, in Section VII, we report the evolution of the effective charges all along the path of atomic displacements from the cubic to the rhombohedral phase and we estimate the spontaneous polarization of the three ferroelectric phase of $BaTiO_3$.

II. THE CONCEPT OF STATIC CHARGE

Intuitively, the atomic charge may first appear as a static concept. The charge associated to an isolated atom is a well-defined quantity. The purpose of defining static atomic charges is therefore to extend this notion to molecules and solids. For these cases, the challenge basically consists to replace the delocalized electronic density by localized point charges associated to each atom. This could *a priori* be performed from electronic density maps obtained experimentally or theoretically. However, as already mentioned by Mulliken [2] in 1935, "there are some difficulties of giving exact definition without arbitrariness for any atomic property". During the seventies, Cochran [1] similarly emphasized that the partition of the electronic distribution into atomic charges can only be done unambiguously when "boundary can be drawn between the ions so as to pass through regions in which the electron density is small compared with the reciprocal of the volume inclosed". This is never the case in practice, and especially when there is appreciable covalent bonding. For most of the solids and molecules, there is consequently no *absolute* criterion to define the static atomic charge and a large variety of distinct definitions have been proposed that are not necessarily quantatively equivalent (see for instance Ref. [3,4]).

As an illustration, different approaches have been considered in order to evaluate the amplitude of the static atomic charges of barium titanate. Some results are summarized in Table I, where different atomic charges are reported in comparison with the nominal charges expected in a purely ionic material (+2 for Ba, +4 for Ti, –2 for O). Some of them were obtained from empirical models; others were deduced from first-principles. The static atomic charges of Ref. [6] were deduced by Harrison within his bond orbital model using universal parameters and neglecting the interactions with the Ba atom. The atomic charges reported by Hewat [17] were approximated from a model initially designed by Cowley [18] for $SrTiO_3$. The charges reported by Khatib *et al.* [19] have been obtained in a shell-model context. In two references, Turik and Khasabov [20,21] estimated the charges from the Madelung constant thanks to a fit of the crystal energy with shell-model parameters. Michel-Calendini *et al.* [22] proposed charges from a population analysis of the $X\alpha$ electronic distribution of a TiO_6 cluster, assuming a charge of +2 on Ba. Cohen and Krakauer [23] deduced the atomic charges from a fit of the DFT-LDA electronic distribution by that of overlapping spherical ions (generated according to the potential induced breathing model) for different ionic configurations. Xu *et al.* [24] reported values deduced from a Mulliken population analysis of a self-consistent OLCAO calculation [25]. In another reference [26], Xu *et al.* proposed different values by integrating the electronic charges in spheres centered on the ions, and partitioning rather arbitrarily the remaining charge outside the spheres following a method proposed in Ref. [27,28].

The results of Table I are not quantitatively identical and illustrate that there is no formal equivalence between the different procedures used to define the atomic charge. However, in agreement with an analysis reported by Meister and Schwartz [4] for the case of molecules, we observe that the values of Table I have some common features, suggesting that the different charges are not independent but should correspond to different scales driven by a common factor.

In particular, all the calculations reveal that the charge transfer from Ti to O is not complete. If $BaTiO_3$ was a purely ionic crystal, the 3d and 4s electrons of Ti would be entirely transferred to the oxygen atoms, yielding a charge of +4 on titanium. However, due for instance to the partial hybridization between O 2p and Ti 3d states [29–35], these electrons remain partly delocalized on the Ti atom so that the static charges on the Ti and O atoms are smaller than they would be in a purely ionic material. This delocalization is illustrated in Figure 1, where we have plotted the partial electronic density associated to the O 2p bands. For the Ba atom, the situation is not so clear than for titanium but most of the studies suggest similarly that the 6s electrons are not fully transferred to the oxygen.

From the previous examples, it is clear that, strictly speaking, the static charge does not give a quantitative information. In the study of mixed ionic-covalent compounds, it remains however a useful concept to discuss qualitatively the transfer of charges from one atom to the other. As a general rule, the partial covalence reduces the amplitude of the static charge. Comparison of a specific static charge in the different phases of a given material or in different compounds can therefore give a relevant information on the evolution of the chemical bond [26].

III. THE CONCEPT OF DYNAMICAL CHARGE

As emphasized by Harrison [6], "whenever an ambiguity arises about the definition of a concept such as the atomic charge, it can be removed by discussing only quantities that can be experimentally determined, at least in principles". If there are some ambiguities to determine the charge to be associated to a given atom, the charge carried by this atom when it is displaced is directly accessible from the induced change of polarization (or dipole moment for molecules). As it is now discussed, the dynamical charges are defined by the change of polarization induced by an atomic displacement; from the viewpoint of Harrison, they appear therefore as more fondamental quantities.

A. Role of the macroscopic electric field

In molecules, the change of dipole moment in direction β (p_β) linearly induced by a small displacement of atom κ in direction α ($\tau_{\kappa,\alpha}$) is uniquely defined. The proportionality coefficient between the dipole moment and the atomic displacement has the dimentionality of a charge and is usually referred to as the *atomic polar tensor* (APT) :

$$Z^*_{\kappa,\alpha\beta} = \frac{\partial p_\beta}{\partial \tau_{\kappa,\alpha}} \tag{1}$$

This concept was introduced by Biarge, Herranz and Morcillo [36–38] for the interpretation of infra-red intensities measurements. Later, Cioslowski [39,40] introduced a scalar charge in connection with this tensor : it is the generalized atomic polar tensor (GAPT) defined as one-third of the trace of the atomic polar tensor.

In periodic systems, equivalent atoms appear in the different unit cells and the definition of the charge can be generalized. A dynamical charge tensor is conventionally defined as the coefficient of proportionality at the linear order between the *macroscopic polarization* per unit cell created in direction β and a rigid displacement of the *sublattice* of atoms κ in direction α, times the unit cell volume Ω_0 :

$$Z^*_{\kappa,\alpha\beta} = \Omega_0 \frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa,\alpha}} \tag{2}$$

We note that $\Omega_0.\mathcal{P}$ can be interpreted as a dipole moment per unit cell. As one κ atom is displaced in each unit cell, in the linear regime, this definition is equivalent to Eq. (1) : it corresponds to the change of dipole moment induced by an isolated atomic displacement. However, contrary to the case of molecules, in macroscopic systems, the previous quantity is not uniquely defined. Indeed, the change of polarization is also dependent on the boundary conditions fixing the macroscopic electric field $\mathcal{E}$ throughout the sample. Basically, we can write :

$$Z^*_{\kappa,\alpha\beta} = \Omega_0 \frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa,\alpha}}\bigg|_{\mathcal{E}=0} + \Omega_0 \sum_j \frac{\partial \mathcal{P}_\beta}{\partial \mathcal{E}_j} \cdot \frac{\partial \mathcal{E}_j}{\partial \tau_{\kappa,\alpha}} \tag{3}$$

As the electrostatics imposes a relationship between macroscopic polarization, electric and displacement fields :

$$\mathcal{D}_\alpha = \mathcal{E}_\alpha + 4\pi\mathcal{P}_\alpha = \sum_j \epsilon^\infty_{\alpha,j}\mathcal{E}_j \tag{4}$$

we can deduce the following equivalent expression :

$$Z^*_{\kappa,\alpha\beta} = \Omega_0 \left.\frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa,\alpha}}\right|_{\mathcal{E}=0} + \Omega_0 \sum_j \frac{(\epsilon^\infty_{\beta,j} - \delta_{\beta,j})}{4\pi} \cdot \frac{\partial \mathcal{E}_j}{\partial \tau_{\kappa,\alpha}}$$

(5)

Depending on the condition imposed on the macroscopic electric field, different concepts have historically been introduced [46].

The *Born effective charge* [5] – alias transverse charge, $Z^{*(T)}$ – refers to the change of polarization that would be observed under the condition of zero macroscopic electric field, so that the second term appearing in the previous equation vanishes :

$$Z^{*(T)}_{\kappa,\alpha\beta} = \Omega_0 \left.\frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa,\alpha}}\right|_{\mathcal{E}=0}$$

(6)

The *Callen charge* [42] – alias longitudinal charge, $Z^{*(L)}$ – is defined from the change of polarization under the condition of zero macroscopic displacement field :

$$Z^{*(L)}_{\kappa,\alpha\beta} = \Omega_0 \left.\frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa,\alpha}}\right|_{\mathcal{D}=0}.$$

(7)

Introducing in Eq. (5) the relationship between field $\mathcal{E}$ and polarization $\mathcal{P}$, deduced from Eq. (4) under the condition of vanishing displacement field, Born and Callen charges can be related to each other thanks to the knowledge of the optical dielectric tensor ϵ^∞ :

$$Z^{*(L)}_{\kappa,\alpha\beta} = Z^{*(T)}_{\kappa,\alpha\beta} - \sum_j \frac{(\epsilon^\infty_{\beta,j} - \delta_{\beta,j})}{4\pi} \cdot 4\pi \underbrace{\Omega_0 \left.\frac{\partial \mathcal{P}_j}{\partial \tau_{\kappa,\alpha}}\right|_{\mathcal{D}=0}}_{Z^{*(L)}_{\kappa,\alpha j}}$$

(8)

so that finally [41] :

$$Z^{*(T)}_{\kappa,\alpha\beta} = \sum_j \epsilon^\infty_{\beta j} \; Z^{*(L)}_{\kappa,\alpha j}$$

(9)

For the case of isotropic materials, we recover the well known equality : $Z^{*(T)}_\kappa = \epsilon^\infty.Z^{*(L)}_\kappa$. Even if they are both related to the change of polarization induced by an atomic displacement, Born and Callen charges appear as two distinct quantities and will be significantly different in materials where ϵ^∞ is different from unity.

Basically, an infinite number of charges could be defined corresponding to different boundary conditions, relating $\mathcal{P}$ and $\mathcal{E}$. One of them is the *Szigeti charge* [43,44] – $Z^{*(S)}$ –, defined as the change of polarization under the condition of vanishing local field, $\mathcal{E}_{loc}$, at the atomic site:

$$Z^{*(S)}_{\kappa,\alpha\beta} = \Omega_0 \left.\frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa,\alpha}}\right|_{\mathcal{E}_{loc}=0}$$

(10)

Contrary to Born and Callen charges, $Z^{*(S)}$ was sometimes considered as a model-dependent concept in the sense that the local field is not observable as the macroscopic field but require some assumptions to be estimated. In the particular case of an isotropic material, the condition of vanishing local field can be written as follows:

$$\mathcal{E}_{loc} = \mathcal{E} + \frac{4\pi}{3}\mathcal{P} = 0$$

(11)

Introducing this condition in Eq. (5) :

$$Z^{*(S)}_\kappa = Z^{*(T)}_\kappa - \frac{(\epsilon^\infty - 1)}{4\pi} \cdot \frac{4\pi}{3} \underbrace{\Omega_0 \left.\frac{\partial \mathcal{P}}{\partial \tau_\kappa}\right|_{\mathcal{E}_{loc}=0}}_{Z^{*(S)}_\kappa}$$

(12)

so that we find :

4

$$Z_\kappa^{*(T)} = \frac{(\epsilon^\infty + 2)}{3} \ Z_\kappa^{*(S)} \tag{13}$$

In calculations of the dynamical properties of crystals, the contribution from the long-range Coulombic interaction to the atomic forces is usually restricted to dipolar forces and is included through a term : $F_\kappa^d = Z_\kappa^{*(T)}\mathcal{E}$. From Eq. (13), it can be checked that this force can be alternatively written in terms of local quantities : $F_\kappa^d = Z_\kappa^{*(S)}\mathcal{E}_{loc}$. In shell-model calculations, this second formulation is usually preferred. Indeed, from its definition, $Z^{*(S)}$ only includes the effects of charge redistribution resulting from short-range interactions and it is therefore conveniently assimilated to the static charge [45,22].

From the previous discussion, it appears that the amplitude of the dynamical charge in macroscopic bodies is sensitive to the condition imposed on the macroscopic electric field. Considering finite clusters of increasing size, we deduce that the amplitude of the dynamical charge, reducing to the APT for a microscopic body, will tend to a different value when the macroscopic limit is taken, depending from the *shape* of the cluster. We investigate now this observation in more details, and provide a unified treatment of dynamical charges in periodic solids and clusters, sufficiently large for the macroscopic quantities $(\mathcal{E}, \mathcal{P}, \epsilon^\infty, ...)$ to be defined.

Following the well-known practice for the study of dielectric bodies [48], we consider that the cluster has a macroscopic ellipsoïdal shape. In this case, the macroscopic field within the cluster present the practical advantage to be homogeneous. In absence of any applied external field, it reduces to the depolarizing field related to the macroscopic polarization thanks to the depolarization coefficients n_α [48] . If we assume in what follows that the principal axes of the ellipsoïd are aligned with the axes of coordinates, we have the following relationship :

$$\mathcal{E}_\alpha = -4\pi n_\alpha \mathcal{P}_\alpha \tag{14}$$

where the geometry imposes : $\sum_i n_i = 1$. Following the same procedure as previously, the dynamical charge $Z^{*(E)}$ of a given atom κ in an ellipsoïd of volume Ω can be written as :

$$Z_{\kappa,\alpha\beta}^{*(E)} = \Omega \ \left. \frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa,\alpha}} \right|_{\mathcal{E}=0} + \Omega \ \sum_j \frac{(\epsilon_{\beta,j}^\infty - \delta_{\beta,j})}{4\pi} \cdot \left. \frac{\partial \mathcal{E}_j}{\partial \tau_{\kappa,\alpha}} \right|_{\mathcal{E}_j=-4\pi n_j \mathcal{P}_j} \tag{15}$$

$$= Z_{\kappa,\alpha\beta}^{*(T)} - \sum_j \frac{(\epsilon_{\beta,j}^\infty - \delta_{\beta,j})}{4\pi} \cdot 4\pi n_j \ \Omega \underbrace{\left. \frac{\partial \mathcal{P}_j}{\partial \tau_{\kappa,\alpha}} \right|_{\mathcal{E}_j=-4\pi n_j \mathcal{P}_j}}_{Z_{\kappa,\alpha j}^{*(E)}} \tag{16}$$

and we have the general relationship :

$$Z_{\kappa,\alpha\beta}^{*(T)} = \sum_j [(\epsilon_{\beta j}^\infty - \delta_{\beta j})n_j + \delta_{\beta j}] \ Z_{\kappa,\alpha j}^{*(E)} \tag{17}$$

In this expression, the presence of the depolarization coefficients emphasizes the influence of the shape of the cluster on the amplitude of $Z^{*(E)}$. The above-mentioned sum rule on the depolarization coefficients forbid to impose the condition of zero electric or displacement fields simultaneously in the three directions. However, we have the following three interesting cases.

First, we consider an extremely oblate ellipsoïdal (slab-like) cluster and take the macroscopic limit. Along the z direction perpendicular to the surface, $n_z \to 1$, while, along the two other directions, $n_x = n_y \to 0$. The dynamical charge for the ellipsoïd is therefore related to the Born effective charge through the following expression:

$$\begin{pmatrix} Z_{\kappa,\alpha x}^{*(T)} \\ Z_{\kappa,\alpha y}^{*(T)} \\ Z_{\kappa,\alpha z}^{*(T)} \end{pmatrix} = \begin{pmatrix} 1 & 0 & \epsilon_{xz}^\infty \\ 0 & 1 & \epsilon_{yz}^\infty \\ 0 & 0 & \epsilon_{zz}^\infty \end{pmatrix} \begin{pmatrix} Z_{\kappa,\alpha x}^{*(E)} \\ Z_{\kappa,\alpha y}^{*(E)} \\ Z_{\kappa,\alpha z}^{*(E)} \end{pmatrix} \tag{18}$$

For uniaxial systems with no off-diagonal terms in the dielectric tensor, we note that the cluster charge along the direction perpendicular to the slab becomes identified with the Callen charge, while that in the slab plane reduces to the Born effective charge.

Differently, for an extremely prolate ellipsoïdal (needle-like) cluster aligned along the z direction (for which $n_z \to 0$ and $n_x = n_y \to 1/2$), we have the following relationship:

$$
\begin{pmatrix} Z_{\kappa,\alpha x}^{*(T)} \\ Z_{\kappa,\alpha y}^{*(T)} \\ Z_{\kappa,\alpha z}^{*(T)} \end{pmatrix} = \begin{pmatrix} \frac{1}{2}(\epsilon_{xx}^{\infty}+1) & \frac{1}{2}\epsilon_{xy}^{\infty} & 0 \\ \frac{1}{2}\epsilon_{yx}^{\infty} & \frac{1}{2}(\epsilon_{yy}^{\infty}+1) & 0 \\ \frac{1}{2}\epsilon_{zx}^{\infty} & \frac{1}{2}\epsilon_{zy}^{\infty} & 1 \end{pmatrix} \begin{pmatrix} Z_{\kappa,\alpha x}^{*(E)} \\ Z_{\kappa,\alpha y}^{*(E)} \\ Z_{\kappa,\alpha z}^{*(E)} \end{pmatrix}
\tag{19}
$$

Here also, the charge along the z direction will reduce to the Born charge in uniaxial systems.

Finally, for a spherical cluster, the symmetry imposes $n_1 = n_2 = n_3 = 1/3$, so that $\mathcal{E}_\alpha = -4\pi\mathcal{P}/3$. For the case of an isotropic material, we recover therefore the condition of vanishing local field and $Z_\kappa^{(E)}$ becomes equivalent to $Z_\kappa^{(S)}$. Therefore, we obtain the interesting result that in isotropic compounds, the Szigeti charge appears as a well-defined quantity and is simply the dynamical charge observed in a spherical cluster.

To summarize, the concept of dynamical charge in macroscopic systems is not uniquely defined : it depends on the relationship between $\mathcal{E}$ and $\mathcal{P}$. In each case, the charge was however expressed in terms of two basic concepts, $Z^{*(T)}$ and ϵ^∞. In this Section, we focused on the term that includes the dielectric constant, and that describes the part of the electronic charge redistribution induced by the presence of a macroscopic field. In the next Section, we will discuss the physical processes responsible of the amplitude of $Z^{*(T)}$.

B. Dynamical changes of orbital hybridizations

During the seventies, a large variety of semi-empirical models were proposed to investigate the underlying physical processes driving the amplitude of dynamical charges. Without being exhaustive, let us mention the interesting treatments of Lucovsky, Martin and Burnstein [49] who decomposed $Z^{*(T)}$ in a local and a non-local contribution, of Lucovsky and White [50] discussing $Z^{*(T)}$ in connection with resonant bonding properties, or the bond charge model of Hübner [51]. The most popular and sophisticated of these approaches remains however that of Harrison [6,52–54] within his bond orbital model (BOM). A similar theory was developed independently by Lannoo and Decarpigny [55].

The BOM basically consists in a simplified tight-binding model, where the Hamiltonian is limited to the on-site and nearest-neighbour terms. The on-site elements are identified to free atom terms value, while the interatomic elements are taken as universal constants times a particular distance dependence. Among other things, these parameters determine the transfer of charge between the interacting atoms. As noted by Dick and Overhauser [56], the charge redistribution produced by the sensitivity of the overlap integrals on the atomic positions is at the origin of an "exchange charge polarization". Similarly, in the Harrison model, the dependence of the parameter on the bond length are at the origin of dynamical transfer of charges and monitors the amplitude of $Z^{*(T)}$ that can become anomalously large as it is illustrated in the following examples.

Let us first consider a diatomic molecule XY, composed of two open shell atoms, where Y has the largest electronegativity. The interatomic distance is u and the dipole moment $p(u)$. These observables allow us to identify a convenient static charge $Z(u) = \frac{p(u)}{u}$, while the dynamical charge is defined as :

$$
\begin{aligned}
Z^*(u) &= \frac{\partial p(u)}{\partial u} \\
&= \frac{\partial}{\partial u}\left(u \cdot Z(u)\right) \\
&= Z(u) + u\frac{\partial Z(u)}{\partial u}
\end{aligned}
\tag{20}
$$

In the last expression, Z^* appears composed of two terms. The first one is simply the static charge. The second corresponds to an additional *dynamical* contribution: it originates in the transfer of charge produced by the modification of the interatomic distance. Within the BOM, this last contribution is associated to off-site orbital hybridization changes and is deduced from the universal dependence of the orbital interaction parameters on the bond length, as illustrated on a practical example in Appendix A. We deduce that the difference between $Z(u)$ and $Z^*(u)$ will be large if $Z(u)$ changes rapidly with u. It can even be non-negligible when $\partial p(u)/\partial u$ is small, if the charge is transferred on a large distance u.

Moreover, this simple model naturally predicts *anomalous* amplitude of the dynamical charges, i.e. a value of $Z^*(u)$ not only larger than the static charge $Z(u)$ but even larger than the "nominal" ionic charge. As the distance between X and Y is modified from 0 to some $\overline{u}$, the distance corresponding to a *complete* transfer of electrons from X to Y, the dipole moment evolves continuously from $p(0) = 0$ (since there is no dipole for that case) to $p(\overline{u})$. Interestingly,

$$
\int_0^{\overline{u}} Z^*(u)\, du = [p(\overline{u}) - p(0)] = \overline{u}\, Z(\overline{u})
\tag{21}
$$

6

so that:

$$\frac{1}{\overline{u}} \int_0^{\overline{u}} Z^*(u)du = Z(\overline{u}) \tag{22}$$

From the last relationship the mean value of $Z^*(u)$ from 0 to $\overline{u}$ is equal to $Z(\overline{u})$ (the "nominal" ionic charge). Consequently, if $Z(u)$ changes with u, $Z^*(u)$ must be larger than $Z(\overline{u})$ for some u between $[0, \overline{u}]$. The difference between $Z^*(u)$ and the nominal charge $Z(\overline{u})$ is usually referred to as the *anomalous* contribution [57].

Switching now from a molecule to a linear chain ...-Y-X-Y-..., and displacing coherently the X atoms by du, shortened and elongated bonds will alternate all along the chain. For Harrison [6], the interaction parameters will be modified such that "the covalent energy increases in the shorted bond, making it less polar by transferring electron to the positive atom". Inversely, electronic charge will be transferred to the negative atom in the elongated bond. These transfers of charge will propagate all along the chain, so that even if the net charge on the atom is not modified, a *current* of electrons will be associated to the atomic displacement. *The direction of this electronic current is opposite to that of the displacement of positive atoms, so that it reinforces the change of polarization associated to this displacement and may generate an anomalously large dynamical charge.* In our example, we have implicitly considered a truly periodic system under the condition of zero macroscopic electric field so that the associated dynamical charge is $Z^{*(T)}$. Under other conditions, the amplitude of the transfers of charge would be additionally influenced by the presence of the field as discussed in the previous Section. We note that, contrary to what was observed for the static charge, consequences of the covalence effects are to increase the amplitude of $Z^{*(T)}$.

The previous model can finally be extended to three dimensional solids. For this case, however, the calculation of the dynamical contribution may become questionable when the identification of the charge transfers is restricted to some specific bonds [58]. As it will be discussed in Sections V and VI the Harrison model remains however a meaningful picture of practical interest to interpret more accurate results.

Up to now, we focused on a "delocalized" model within which the electronic charge redistribution induced by an atomic displacement is visualized by transfer of charge induced by *off-site* changes of hybridization. In the past, various shell-models have however also been developed to investigate the dynamical properties of crystals. In these calculations, an accurate description of $Z^{*(T)}$ was mandatory in order to reproduce correctly the splitting between longitudinal and transverse optic modes in the vicinity of the Γ point. Contrary to the BOM, the shell-model is "local" and treats the charges within the Clausius-Mosotti limit. The previous dicussion in terms of a static and dynamical contribution to $Z^{*(T)}$ remains valid. However, the dynamical contribution results there simply from the relative displacement of the shell charge as a whole with respect to the atom. It is attributed to the polarizability of the electrons in the local field at the atomic site. In the language of the BOM, such a displacement of the electronic cloud can be understood in terms of *on-site* changes of hybridizations. This approach contrasts with the model developped by Harrison but can also yield plausible Born effective charge amplitudes /citeGhosez95b.

It must be emphasized that it is not possible to discriminate *a priori* between localized and delocalized models. Within the recent theory of polarization, it has been clarified that for the purpose of understanding polarization problems, "the true quantum mechanical electronic system can be considered as an effective classical system of quantized point charges, located at the centers of gravity associated with the occupied Wannier functions in each unit cell" [59]. Consequently, the correct description of the Born effective charges does not require to reproduce correctly all the features of the valence charge distribution but *only* the displacement of its Wannier center (see Ref. [60]). As schematized in Fig. 2, antagonist models can reproduce a similar displacement of the Wannier center. In real materials, both local polarizability and transfers of charge do probably contribute to the charge reorganisation. It will be emphasized later how first-principles investigations can help to identify the dominant mechanism.

In conclusion, this Section has shown that Z^* is related to the static charge (see Eq. 20) but does not restrict to it: Z^* may also include an additional, important, dynamical contribution. Whatever the mechanism of the charge redistribution (localized or delocalized), the amplitude of the dynamical contribution cannot be estimated from the inspection of the electronic density alone. So, we partly disagree with Meister and Schwarz [4] who suggested that all the charges *including* the GAPT are driven by the same underlying parameter. In what follows, based on firs-principles calculations, we illustrate on different examples that $Z^{*(T)}$ may become anomalously large and independent of the amplitude of the static charge Z. Moreover, two atoms with similar Z can also exhibit strongly different $Z^{*(T)}$.

IV. A FIRST-PRINCIPLES APPROACH

A brief review of the most commonly used first-principles approaches for computing the Born effective charges has been reported recently [60]. Going beyond semi-empirical approaches, *ab initio* techniques allow accurate prediction

of $Z^{*(T)}$ in materials where its amplitude is not necessarily directly accessible from the experiment. Going further, the first-principles approaches are also offering a new opportunity to clarify the microscopic mechanism modulating the amplitude of $Z^{*(T)}$ without any preliminary hypothesis. As it will be illustrated in the following sections, it reveals particularly useful to understand the origin of anomalously large $Z^{*(T)}$ in ABO_3 compounds.

The results of the present paper have been obtained in the framework of the density functional formalism [62,63]. The exchange-correlation energy has been evaluated within the local density approximation, using a Padé parametrization [64] of Ceperley-Alder homogeneous electron gas data [65]. Integrals over the Brillouin-zone were replaced by a sum on a mesh of $6 \times 6 \times 6$ special **k**-points [66,67] (10 points in the irreducible Brillouin zone). The "all electron" potentials were replaced by the same ab initio, separable, extended norm-conserving pseudopotentials as in Ref. [12]. The wavefunctions were expanded in plane waves up to a kinetic energy cutoff of 35 Hartree (about 4100 plane waves).

The Born effective charges have been deduced from linear response calculations [7], using a variational formulation [8,68,69] to the density functional perturbation theory. The decomposition of individual contributions from separate groups of occupied bands has been performed following the scheme described in Ref. [60]. The parameters used for the calculations guarantee a convergency better than 0.5% on $Z^{*(T)}$ as well as on each of its band-by-band contributions.

V. THE CUBIC PHASE OF ABO_3 COMPOUNDS

A. General results

Recently, the Born effective charge tensors of perovskite ABO_3 compounds have been at the center of numerous investigations [11–15,61,70–73]. In the cubic phase, they are fully characterized by a set of four independent numbers. The charge tensor of the A and B atoms is isotropic owing to the local spherical symmetry at the atomic site. For oxygen, the local environment is tetragonal and two independent elements $O_\parallel$ and $O_\perp$ must be considered, referring respectively to the change of polarization induced by an atomic displacement parallel and perpendicular to the B-O bond. In Table II, we summarize the results obtained within different approaches for the cubic phase of $BaTiO_3$.

The first reliable estimation of $Z^{*(T)}$ in $BaTiO_3$ is probably due to Axe [10], from empirical fitting to experimental mode oscillator strengths [74]. In ABO_3 compounds, $Z^{*(T)}$ cannot be determined unambiguously from the experiment. However, within some realistic hypothesis, Axe identified the independent elements of the effective charges of $BaTiO_3$ and already pointed out their two essential features. First, the oxygen charge tensor is highly anisotropic. Second, the charges on Ti and $O_\parallel$ contain a large *anomalous* contribution (i.e. an additional charge with respect to the nominal ionic value of +2 for Ba, +4 for Ti and -2 for O).

Both these characteristics are confirmed by the first-principles calculations. Our ab initio results, computed from linear response, are also in excellent agreement with those of Zhong *et al.* [13], obtained from finite differences of polarization. The charge neutrality sum rule, reflecting the numerical accuracy of our calculation, is fulfilled to within 0.02. We note that the values of $Z^{*(T)}$ are also qualitatively reproduced from a shell-model calculation [61] and accurately predicted within the SCAD model [77].

The anomalous amplitude of the dynamical charge, reported in this Section, is not a specific feature of $BaTiO_3$. Similar computations of $Z^{*(T)}$ were performed on different perovskite ABO_3 compounds and they all reproduce the same characteristics than in $BaTiO_3$. A non exhaustive list of these results is reported in Table III. We observe that the choice of the A atom has a rather limited influence on $Z_B^{*(T)}$ and $Z_{O\parallel}^{*(T)}$, which appear closely related to the B atom. While the nominal ionic charge of Ti and Zr is +4 in these compounds, the Born effective charge is between +7.08 and +7.56 for Ti, and approximately equal to +6.03 for Zr. For Nb, the ionic charge is +5, while the Born effective charge is between +9.11 and +9.37. Extending the investigations to WO_3 in the reference cubic phase (defect perovskite structure), the ionic charge on W is equal to +6, while the Born effective charge reaches the much larger value of +12.51. For the class of perovskite ABO_3 compounds, it can be checked that $Z_B^{*(T)}$ evolves quasi linearly with the nominal charge of the B atom [78].

For materials containing Pb, the previous considerations remain valid but there are additional anomalies concerning $Z_A^{*(T)}$ and $Z_{O\perp}^{*(T)}$. This feature is due to the more covalent bonding of lead with oxygen that was illustrated in Ref. [35,84]. In what follows, we will not be concerned with these lead compounds.

B. Origin of the anomalous contributions

The approximate reciprocity between $O_\parallel$ and B anomalous contributions suggests that they should originate in a global transfer of charge between B and O atoms as described in Section III B. In Ref. [6], Harrison had in fact already suggested the existence of giant Born effective charges in perovskite materials. Being unaware of the earlier results of Axe, he had however no experimental evidence to corroborate his semi-empirical calculations.

In Appendix A, we report results obtained within the Harrison model (it follows the method described for KCl in Ref. [6], p. 334.). For $SrTiO_3$, from the universal tight-binding parameters of Harrison, we get a value of -8.18 for $Z_{O_\parallel}^{*(T)}$, making plausible the giant anomalous effective charges only by focusing on the dynamical changes of hybridization between occupied O 2s–O 2p states and the unoccupied metal d states. In $BaTiO_3$, the hybridization between O 2p and Ti 3d orbitals is a well known feature, confirmed by various sources (experiments [29,30], LCAO calculations [31–33] and DFT results [34,35]). In this context, it was therefore realistic to focus on O 2p - B d hybridization changes to explain intuitively large anomalous contributions [13].

At the opposite, it may therefore appear surprising that model calculations which does *not* explicitly include transfer of charges are able to predict correctly the amplitude of the Born effective charges. For instance, in Table I, we observe that the values of $Z^{*(T)}$ are qualitatively reproduced by a shell-model calculation [61]. A similar agreement between *ab initio* and shell model results was highlighted for $KNbO_3$ [80]. In both cases, the calculation was performed within the "polarizability model" introduced by Bilz *et al.* [79], which includes an anisotropic and non-linear polarizability of the O atoms. In the same spirit, at the level of the SCAD model, the Born effective charges are accurately reproduced while there is no explicit transfer of electrons between the different atomic sites. As discussed in Section III, antagonist models can be invoked to explain the origin of anomalous contributions as soon as they globally reproduce a similar displacement of the Wannier center of the valence charge distribution. What appear as a macroscopic current along the Ti–O chain within the BOM shows itself as an unusual polarizability of the oxygen atoms within the shell model.

It was not possible to discriminate unambiguously between localized and delocalized model until Posternak *et al.* [15] proposed a convincing proof of the crucial role of "off-site" hybridizations. Based on first-principles calculations, they demonstrated for $KNbO_3$ that the anomalous contribution to the charge of Nb and $O_\parallel$ disappears if the hybridization between O 2p and Nb 4d orbitals is artificially suppressed. In a similar spirit, the inspection of the Wannier functions of $BaTiO_3$ and the analysis of their deformation under an atomic displacement reported by Marzari and Vanderbilt [81] confirm the predominant role played by the Ti 3d orbitals and the explanation introduced by Harrison.

In the next Section, we propose a band-by-band decomposition of the Born effective charges [14,61]. This technique appears as a tool of paramount importance to clarify the microscopic origin of anomalous contributions. Identifying the dynamical transfer of charges without any preliminary hypothesis on the orbitals that interact, it will allow to generalize the basic mechanism that was proposed by Harrison.

VI. IDENTIFICATION OF DYNAMICAL CHANGES OF HYBRIDIZATION

In ABO_3 compounds, the electronic band structure is composed of well separated sets of bands. The hybridizations between the orbitals of the different atoms are relatively small and each band can be identified by the name of the main atomic orbital which contributes to this energy level in the solid. The Born effective charge is defined by the change of polarization associated to a specific atomic displacement. Our purpose will be to identify the contribution of each well separated set of bands to this change of polarization [14,61].

A. Reference configuration

In Ref. [60], we have described how band-by-band contributions to $Z^{*(T)}$ can be separated from each others. Moreover, it has been demonstrated that the contribution to $Z_{\kappa,\alpha\beta}^{*(T)}$ from a single occupied band n can be interpreted as a change of polarization $\Omega_o \Delta \mathcal{P}_\beta = -2.\Omega_o \Delta d_\beta$ where Δd_β is the displacement in direction β of the Wannier center of band n, induced by the unitary displacement of the sublattice of atoms κ in direction α.

In order to understand the origin of the displacement of the Wannier center of each band, it is helpful to define a *reference* configuration that corresponds to what we would expect in a purely ionic material. In such fictitious material, each band would be composed of a single non-hybridized orbital and the Wannier center of each band would be centered on a given atom. In absence of any hybridization, when displacing a given sublattice of atoms κ, the Wannier center of the bands centered on the moving atoms would remain centered on it, while the position of the

center of gravity of the other bands would remain unaffected. The contributions of these two kind of bands to $Z_\kappa^{*(T)}$ would therefore be -2 and 0 electrons, respectively.

In the real material, the *anomalous* contribution of a particular band m to a given atom κ is defined as the additional part with respect to the reference value expected in absence of any hybridization: it reflects how the center of the Wannier center of band m is displaced relatively to the atoms when the sublattice κ moves [82]. Considering each band as a combinaison of atomic orbitals, such a displacement of the Wannier center of a band with respect to its reference position *must* be attributed to hybridization effects: it is associated to the admixture of a new orbital character to the band. When the orbitals which interact are located on different atoms ("off-site" hybridization), the dynamical changes of hybridization can be visualized as transfers of charge. If the interacting orbitals are on the same atom ("on-site" hybridization), the mechanism much looks like a polarizability.

Rigorously, our band-by-band decomposition is performed within DFT and formally only concerns the Kohn-Sham particles. It seems however that the results are rather independent of the one-particle scheme [83] used for the calculation so that the results presented here should give a good insight on the physics of the ABO_3 compounds.

B. $BaTiO_3$

Let us first applied the band-by-band decomposition to barium titanate. The band structure of $BaTiO_3$ is presented in Fig. 3. Results of the decomposition of $Z^{*(T)}$ in the theoretical cubic structure of $BaTiO_3$ are reported in Table IV. The first line (Z_κ) brings together the charge of the nucleus and core electrons included in the pseudopotential. The other contributions come from the different valence electron levels. The sum of the band-by-band contributions on one atom is equal to its global effective charge while the sum of the contribution to a particular band from the different atoms is equal to -2 (within the accuracy of the calculation), the occupancy of this band.

Focusing first on the titanium charge, we observe that the Ti $3s$ contribution (-2.03) is close to -2, confirming that the Ti $3s$ electrons follow the Ti atom when moving, independently from the change of its surrounding. This result *a posteriori* justifies the inclusion of deeper electronic levels as part of the ionic pseudopotentials. At the opposite, it is shown that the giant anomalous charge of titanium essentially comes from the O $2p$ bands ($+2.86$). It corresponds to a displacement of the Wannier center of the O $2p$ bands in opposite direction to the displacement of the Ti atom. This observation is in perfect agreement with the Harrison model: it can be understood by dynamical changes of hybridization between O $2p$ and Ti $3d$ orbitals, producing a transfer of electron from O to Ti when the Ti-O distance shortens. This explanation was confirmed recently from the inspection of the O $2p$ Wannier functions [81]. Beyond the previous observations, we note however that there are also small anomalous charges from the Ti $3p$, O $2s$ and Ba $5p$ bands. These contributions are not negligible. The positive anomalous charges correspond to a displacement of the center of the Wannier function of the O and Ba bands in the direction of the closest Ti when this atom has moved. Some of these features go beyond the Harrison model, within which anomalous contributions to $Z_{Ti}^{*(T)}$ in Table IV would be restricted to the O $2p$ and O $2s$ bands. They suggest other kind of hybridization changes, that will be now more explicitly investigated.

Focusing on barium, the global anomalous effective charge ($+0.77$) is small compared to that of Ti and this feature was first attributed to its more ionic character [13]. This ionicity is inherent to the Harrison model [6] and was confirmed in some ab initio studies [35,84]. Surprisingly, our decomposition reveals however that the anomalous charges of the O $2s$ ($+0.73$) and O $2p$ ($+1.50$) bands are not small at all. They are nevertheless roughly compensated by another Ba $5s$ ($+0.11$)and Ba $5p$ ($+1.38$) anomalous contributions. This result suggests that there are dynamical changes of hybridization between Ba and O orbitals as it was the case between O and Ti, except that the mechanism is here restricted to *occupied* states. *This basically corresponds to a unitary transform within the subspace of the occupied states which is unable to displace the global Wannier center of the valence charge.* Our result so supports the hybridization of Ba orbitals, in agreement with experiment [29,30], LCAO calculations [32,33] and DFT [34] computations. Similar compensating contributions were recently observed in ZnO which has conventional Born effective charges [83] and in a series of alkaline-earth oxides [85].

We note that a confusion sometimes appears that should be removed: the *amplitude* of the anomalous contributions to $Z^{*(T)}$ is not related to the amplitude of the hybridizations but to the *rate of change* of these hybridizations under atomic displacements. It is clear that, in $BaTiO_3$, the Ba $5p$ contribution to the O $2p$ bands is smaller than the contribution from the Ti $3d$ orbitals [34,35]. However, the high sensitivity of this relatively weak covalent character under atomic positions is sufficient to produce large band by band anomalous contributions to $Z^{*(T)}$. From that point of view, the Born effective charge appears therefore as a sensitive tool to identify the presence of even small hybridizations.

Finally, concerning the oxygen, even if $O_\parallel$ and $O_\perp$ are defined respectively for a displacement of O in the Ti and Ba direction, it seems only qualitative to associate $Z^{*(T)}_{O_\parallel}$ with $Z^{*(T)}_{Ti}$ and $Z^{*(T)}_{O_\perp}$ with $Z^{*(T)}_{Ba}$ as suggested in Ref. [13]. The O 2p anomalous contributions to Ti and $O_\parallel$ do not exactly compensate. Moreover, O 2p contribution to $Z^{*(T)}_{Ba}$ does not come from $O_\perp$ only but has equivalent contributions from $O_\parallel$. This seems to confirm the idea of Bennetto and Vanderbilt [58] that in 3D materials, transfers of charges are not necessarily restricted to a particular bond, but is a rather complex mechanism that must be treated as a whole.

To summarize, our study has clarified the mixed ionic-covalent character of BaTiO$_3$: it clearly establishes that the covalent character is not restricted to the Ti-O bond but also partly concerns the Ba atom. Moreover, it leads to a more general issue. It illustrates that *the presence of a large anomalous charge requires a modification of the interactions between occupied and unoccupied electronic state. The contributions originating from the change of the interactions between two occupied states correspond to unitary transforms within the subspace of the valence charge : they compensate, and do not modify the global value of $Z^{*(T)}$.*

C. SrTiO$_3$

The same analysis is now performed on SrTiO$_3$. Its band structure (Fig. 4) is very similar to that of BaTiO$_3$, except that the Ti 3p and Sr 4s bands are energetically very close to each others. Consequently, they strongly mix and it should be relatively meaningless to separate their respective contributions. The Sr 4p and O 2s states are in the same energy region but can be separated, contrary to what was observed in a study of SrO [85].

The result of the decomposition is very similar (Table V) to that reported for BaTiO$_3$. There is still a giant contribution to $Z^{*(T)}_{Ti}$ from the O 2p bands. On the other hand, while the Ba 5p bands were approximately centered between O 2s and O 2p bands in BaTiO$_3$, the Sr 4p electrons are closer to the O 2s bands and mainly hybridize with them in SrTiO$_3$. This phenomenon produces large but compensating contributions from Sr 4p and O 2s bands to $Z^{*(T)}_{Sr}$. Such an evolution is in agreement with the picture that anomalous contributions originate from off-site orbital hybridization changes.

D. Other examples

From the two previous results that concern two very similar materials, it might be suggested that not only the dynamical hybridization of the valence bands with unoccupied d-states but also the particular cubic perovskite structure of ABO$_3$ compounds plays a major role in determining $Z^{*(T)}$. For instance, the anomalous charge could partly originate in the local fields at the atomic sites, known to be anomalously large in this structure [87]

It is interesting to observe that anomalous charges are not restricted to perovskite solids but were also detected in a series of alkaline-earth oxides of rocksalt structure (CaO, SrO, BaO) [88,85] or even Al$_2$Ru [89,90], all examples where the unoccupied d-states seem to play a major role. Interestingly, two materials belonging to the same structure can present completely different charges. This was illustrated for the case of TiO$_2$ rutile and SiO$_2$ stishovite [91,92]: while relatively conventional charges were observed on Si (+4.15) and O (-2.46) along the Si-O bond in stishovite, giant effective charges, similar to those of BaTiO$_3$, were obtained on Ti (+7.33) and O (-4.98) along the Ti-O bond in rutile. Similarly, no anomalous charge was reported for MgO ($Z^{*(T)}_O = -2.07$), presenting the same rocksalt structure than BaO ($Z^{*(T)}_O = -2.80$) [85]. In the same spirit, the same atom in different environments can present similar dynamical charge, as illustrated for $Z^{*(T)}_{Ti}$ in BaTiO$_3$ and TiO$_2$ [92], or for $Z^{*(T)}_{Zr}$ in BaZrO$_3$ [13] and ZrO$_2$ [93]. Also, in the family of ABO$_3$ compounds, giant effective charges are observed on Ti in CaTiO$_3$ ($Z^{*(T)}_{Ti} = 7.08$, [13]) but not on Si in CaSiO$_3$ ($Z^{*(T)}_{Si} = 4.00$, [94]).

We observe that the presence of partly hybridized d-states seems the only common feature between the materials presenting giant anomalous effective charges, listed up to date. This feature finds a basic justification within the BOM of Harrison: the interaction parameters involving d-states are indeed much more sensitive to the interatomic distance than those involving, for example, s and p orbitals [6]: They will therefore be associated to larger dynamical transfer of charge and will generate higher $Z^{*(T)}$.

VII. SENSITIVITY OF $Z^{*(T)}$ TO STRUCTURAL FEATURES

In the litterature, calculations of $Z^{*(T)}$ essentially focused on the cubic phase of ABO$_3$ compounds [11–15,61,70,71]. On the basis of an early study of KNbO$_3$ [11], it was concluded that the Born effective charges are independent of the ionic ferroelectric displacements (i.e. they remain similar in the different phases). Another investigation in the tetragonal phase of KNbO$_3$ and PbTiO$_3$ [13], seemed to confirm that $Z^{*(T)}$ are quite insensitive to structural details.

These results were surprising if we remember that anomalous contributions to $Z^{*(T)}$ are closely related to orbital hybridizations, these in turn, well known to be strongly affected by the phase transitions [35,84]. We will see in this Section that, contrary to what was first expected, Born effective charges in BaTiO$_3$ are strongly dependent of the structural features.

We first investigate the sensitivity of the Born effective charges to the ferroelectric atomic displacements [61]. For that purpose, we compute $Z^{*(T)}$ in the three ferroelectric phases at the experimental unit cell parameters, with relaxed atomic positions as reported in Ref. [95]. Table VI summarizes the results for a cartesian set of axis where the z-axis points in the ferroelectric direction. The Ba and Ti charge tensors are diagonal in each phase for this particular choice. In the case of O, we note the presence of a small asymmetric contribution for the lowest symmetry phases. The eigenvalues of the symmetric part of the tensor are also reported. In each phase, the eigenvector associated to the highest eigenvalue of O approximately points in the Ti-O direction and allows to identify the highest contribution as O$_\parallel$. The other eigenvalues can be referred to as O$_\perp$, by analogy with the cubic phase.

Although the charges of Ba and O$_\perp$ remain globally unchanged in the 4 phases, strong modifications are observed for Ti and O$_\parallel$: for example, changing the Ti position by 0.076Å (2% of the unit cell length) when going from the cubic to the rhombohedral phase, reduces the *anomalous* part of $Z^{*(T)}_{Ti}$ by more than 50% along the ferroelectric axis (Table VI). Equivalent evolutions are observed in the other ferroelectric phases. Similar changes were detected in KNbO$_3$ [72].

In the isotropic cubic structure, Harrison had explained the large value of $Z^{*(T)}$ in terms of the Ti-O bond length. For the anisotropic ferroelectric phases, it should be intuitively expected that the shortest Ti-O distance d_{min} in the structure will dominate the bonding properties. It is therefore tempting to transpose the Harrison model to understand the evolution of $Z^{*(T)}$ in terms of the distance d_{min}. In Fig. 5, the amplitude of $Z^{*(T)}_{Ti}$ in the direction of the shortest Ti-O bond length of each phase is plotted with respect to d_{min}. I similar graph can be obtained for O. For the different phases, at the experimental lattice parameters, we observe that the anomalous parts evolve quasi linearly with d_{min}.

Independently from the previous calculations, we also investigated the evolution of $Z^{*(T)}$ under isotropic pressure (Table VII). In contrast with the changes observed with respect to the atomic displacements, the charge appears essentially insensitive to isotropic compression. In particular, in the compressed cubic cell at 3.67 Å where the Ti-O distance is *the same* that the shortest Ti-O bond length in the tetragonal structure [97], $Z^{*(T)}_{Ti}$ remains very close to its value at the optimized volume. This new element clearly invalidates the expected dependence from $Z^{*(T)}$ to d_{min}.

The fundamental difference between the cubic and tetragonal structures lies in the fact that in the cubic phase every Ti-O distance is equal to the others, while in the tetragonal phase, along the ferroelectric axis, a short Ti-O bond length (d_{min}) is followed by a larger one (d_{max}) which *breaks* the Ti-O chain in this direction. In order to verify that it is not this large Ti-O distance which, alternatively to d_{min}, is sufficient to inhibit the giant current associated to the anomalous charges, we also performed a calculation in an expanded cubic phase where $a_o = 2.d_{max}$: we observe however that the Ti charge is even larger than in the optimized cubic phase.

We conclude from the previous investigations that *the amplitude of $Z^{*(T)}$ in BaTiO$_3$ is not dependent on a particular interatomic distance (d_{min}, d_{max}) but is more critically affected by the anisotropy of the Ti environment along the Ti–O chains*. In agreement with this picture, Wang *et al.* [72] reported recently an insensitivity of $Z^{*(T)}$ to a tetragonal macroscopic strain in KNbO$_3$. Also, the charges reported by Bellaiche *et al.* [96] in mixed a compound as PZT, where the ionic environment becomes anisotropic, seem to confirm our results.

A band by band decomposition of $Z^{*(T)}_{Ti}$ (Table VIII) points out that the difference between the cubic and tetragonal phases is essentially localized at the level of the O 2p bands (+1.48 instead of +2.86) while the other contributions remain very similar. This suggests an intuitive explanation. In the cubic phase the O 2p electrons are widely delocalized and dynamical transfer of charge can propagate along the Ti-O chain as suggested by Harrison. In the tetragonal phase, the Ti-O chain behaves as a sequence of Ti-O dimers for which the electrons are less polarizable. This smaller polarizability is confirmed by a similar reduction of the optical dielectric constant along the ferroelectric direction. This analysis seems plausible from the Wannier function analysis reported recently by Marzari and Vanderbilt [81].

Finally, let us mention that if the evolution of $Z^{*(T)}$ is relatively weak under isotropic pressure, it would be wrong to consider that the dynamical properties of BaTiO$_3$ are insensitive to the volume: small changes are observed that are

of the same order of magnitude than for other compounds like SiC [98,99]. The direction of the evolution is however different. Moreover, the evolution of the different charges is even not identical: while the absolute value of $Z_{Ba}^{*(T)}$ and $Z_{O\perp}^{*(T)}$ decreases with increasing volume, the inverse behaviour is observed for $Z_{Ti}^{*(T)}$ and $Z_{O\parallel}^{*(T)}$.

Here also, the band by band decomposition (Table IX) reveals some hidden features. In the compressed cubic phase, the anomalous part of the Ba 5p , Ba 5s and Ti 3p bands are 50% larger than in the optimized cubic cell. This suggests an evolution of the interactions between occupied orbitals that is coherent with the modification of the interatomic short-range forces observed independently [16]. At the opposite, in our expanded cubic phase, most of the anomalous contributions to $Z_{Ba}^{*(T)}$ and $Z_{Ti}^{*(T)}$ have disappeared in agreement with the picture of a more ionic material. The O 2p contribution, is the only one that remains surprisingly large. Comparing to the value obtained for the cubic phase at the experimental volume, its evolution was even more important than the linear dependence upon the bond length, expected from the Harrison model.

VIII. SPONTANEOUS POLARIZATION

The spontaneous polarization (P_s) of the ferroelectric phases can be determined by integrating the change of polarization along the path of atomic displacement from the paraelectric cubic phase (taken as reference) to the considered ferroelectric structure. If the effective charges were roughly constant, this integration should be approximated by:

$$P_{s,\alpha} = \frac{1}{\Omega_o} \sum_{\kappa,\beta} Z_{\kappa,\alpha\beta}^{*(T)} \, \delta\tau_{\kappa,\beta} \tag{23}$$

However, we have seen, in the previous Section, that the Born effective charges are strongly affected by the atomic displacements. It is therefore important to investigate their evolution all along the path of atomic displacements from one structure to the other.

We performed the calculation for a transformation from the cubic to the rhombohedral structure. The rhombohedral macroscopic strain is very small and was neglected [100] : our calculation was performed by displacing the atoms to their theoretically optimized position in rhombohedral symmetry, when keeping the cubic lattice parameters. The result is reported in Figure 6, for $Z_{Ti}^{*(T)}$ along the ferroelectric direction. A similar curve can be obtained for $Z_{O\parallel}^{*(T)}$. We observe that the evolution of $Z^{*(T)}$ is approximately quadratic close to the cubic phase. However, it becomes rapidly linear, and remains linear for displacements even larger than those associated to the ferroelectric distortion.

Expecting a similar evolution of the dynamical charges for the tetragonal and orthorhombic displacements, an estimation of the spontaneous polarization in the ferroelectric phases can be found when using Eq. (23) with a mean effective charge determined from its value in both phases. Using a mean charge estimated from the values in the para- and ferro-electric phases, we obtain the spontaneous polarizations presented in Table X.

Our results are only in relative agreement with the experiment [101,17] and suggest different comments. Firstly, we would like to mention that part of the discrepancy must be assigned to the theoretical overestimation of the computed ferroelectric displacements, discussed in Ref. [95] : when using the experimental displacements of Ref. [102], we recover a better estimation of P_s as in Ref. [13]. The dispersion of X-rays diffraction data makes however difficult the exact identification of the ferroelectric displacements. Secondly, another part of the error could be due to the lack of polarization dependence of the LDA [103]. Finally, we note that there is also some uncertainty on the experimental value of P_s.

IX. CONCLUSIONS

In this paper, we first analyzed the links between different definitions of atomic charge. We have shown that, contrary to the static definitions, dynamical effective charges also depend on the electronic charge reorganisation induced by an atomic displacement. The amplitude of this dynamical contribution is monitored not only by the bonding with the other atoms but also, for large systems, by the condition imposed on the macroscopic electric field. A unified treatment of the concept of dynamical charge in molecules, large clusters, and truly periodic systems has been presented, in which the Born effective charge and the optical dielectric constant appear as the two fundamental quantities. The microscopic origin of the dynamical contribution has been discussed in terms of local polarizability and delocalized transfers of electrons.

Based on various first-principles results, we have then emphasized that the Born effective charges are anomalously large in the family of ABO_3 compounds: their amplitude can reach more than twice that of the nominal ionic charges. This feature was explained in terms of interatomic transfers of charge, produced by "off-site" dynamical changes of hybridization. For $BaTiO_3$ and $SrTiO_3$, we have brought to light complex dynamical changes of hybridization, concerning not only Ti and O but also Ba and Sr orbitals. The hybridizations restricted to occupied states generate however compensating anomalous contributions so that, finally, the total value of $Z^{*(T)}$ is essentially affected by dynamical changes of hybridization between O 2p and Ti 3d orbitals.

As a more general issue, it appears that the existence of partial hybridizations between occupied and unoccupied states is an important feature for candidate to large anomalous Born effective charges. Moreover, the dynamical transfers of charge are expected to be larger when such a hybridization involve d states, for which the interactions parameters with other orbitals are particularly sensitive to the interatomic distance.

Investigating the evolution of $Z^{*(T)}$ to the structural features, we have shown that they are strongly affected by the ferroelectric atomic displacements and much less sensitive to isotropic pressure. The results have clarified that the amplitude of $Z^{*(T)}$ is not monitored by a particular interatomic distance but is dependent on the anisotropy of the Ti environment along the Ti-O chains.

Finally, the effective charges were used to estimate the spontaneous polarization in the ferroelectric phases of $BaTiO_3$. For that purpose, their evolution was investigated all along the path of atomic displacement from the cubic to the rhombohedral structure.

All along this work, we only focused on the *microscopic* mechanisms that govern the amplitude of the Born effective charges. In independent studies, it was also emphasized that the anomalously large Born effective charges produce a giant LO-TO splitting in ABO_3 compounds, specially for the ferroelectric phonon mode [13,16]. Moreover, it was demonstrated that this feature is associated to the existence of an anomalously large destabilizing dipole-dipole interaction, sufficient to compensate the stabilizing short-range forces and induce the ferroelectric instability [16]. In materials where polar modes play a major role, the Born effective charge appears therefore also as a "key concept" to relate the electronic and structural properties [104].

ACKNOWLEDGMENTS

APPENDIX A: THE HARRISON MODEL

In this Appendix, we briefly describe the bond-orbital model proposed by Harrison for the case of ABO_3 compounds [6]. In particular, we pay a particular attention to the definition and the calculation of static and dynamical charges within this model. Values are reported for $SrTiO_3$.

The bond orbital model of Harrison consists in a simplified tight-binding model, where the Hamiltonian is limited to the on-site and nearest-neighbour terms. Moreover, for ABO_3 compounds, it is assumed that the A atom has no other function than to provide electrons to the system, and is fully ionized. The only considered interactions involve B and O atom orbitals.

The model includes O 2s, O 2p and B d orbitals, interacting through $V_{sd,\sigma}$, $V_{pd,\sigma}$ and $V_{pd,\pi}$ parameters. As the matrix elements $V_{sd,\sigma}$ and $V_{pd,\sigma}$ are nearly identical, it is suggested to construct two sp hybrids on the oxygen, $|h_\pm> = (|s> \pm |p>)/\sqrt{2}$. Each of these hybrid will have a large matrix element ($V_{hd,\sigma}^+ = [V_{sd,\sigma} + V_{pd,\sigma}]/\sqrt{2}$) coupling it to the d state on one side and a negligible matrix element ($V_{hd,\sigma}^- = [V_{sd,\sigma} - V_{pd,\sigma}]/\sqrt{2}$) coupling it to the d state on the other.

1. Effective static charge

In absence of orbital interactions, the static charges of $SrTiO_3$ would be of $+2$ on Sr, $+4$ on Ti and -2 on O. However, due to the Ti-O orbital interactions, the transfer of electrons from Ti to O is not complete. Within the BOM, the effective static charge on O can be estimated as:

$$Z_O = -2 + T_\sigma + T_\pi \tag{A1}$$

where

$$T_\sigma = 4\left(\frac{V_{hd,\sigma}^+}{[\epsilon_d - (\epsilon_s + \epsilon_p)/2]}\right)^2 \tag{A2}$$

("4" because there are 2 hybrids composed of 2 electrons that each interacts mainly with one Ti neighbour) and

$$T_\pi = 8\left(\frac{V_{pd,\pi}^+}{[(\epsilon_d - \epsilon_p)]}\right)^2 \tag{A3}$$

("8" because there are 4 electrons that are each partly delocalized on the 2 Ti neighbours).

For $SrTiO_3$, from the parameters of Matheiss (Ref. [6], p. 445), $T_\sigma = 0.35$ and $T_\pi = 0.68$ so that the effective static charge on the oxygen atom is $Z_O = 0.96$.

2. Born effective charge

Following the discussion of Section III-B, the Born effective charge can be obtained by adding to the static charge the dynamical contribution originating in the dependence of the matrix elements V upon the interatomic bond length d. From Harrison's Solid State Table (see also Eq. (19-11) in Ref. [6]), the previous matrix elements have all the same interatomic dependence:

$$V = Kd^{-7/2} \tag{A4}$$

$$\delta V = -\frac{7}{2}V\frac{\delta d}{d} \tag{A5}$$

so that

$$(V + \delta V)^2 = V^2 + 2\,V\,\delta V + \mathcal{O}(\delta V^2) \tag{A6}$$

$$= V^2 + 2\,(\frac{-7}{2})V^2\frac{\delta d}{d} + \mathcal{O}(\delta V^2) \tag{A7}$$

When displacing the O atom along the Ti-O direction, there will be an additional transfer of electron from O to the nearest Ti that is equal to

$$\delta T_\sigma = 2[2\,(\frac{-7}{2})(\frac{V_{hd,\sigma}}{\epsilon_d - \epsilon_h})^2]\frac{\delta d}{d} \tag{A8}$$

$$\delta T_\pi = 4[2\,(\frac{-7}{2})(\frac{V_{pd,\pi}}{\epsilon_d - \epsilon_p})^2]\frac{\delta d}{d} \tag{A9}$$

On the other hand, there will be the same transfer of charge from the other neighbour Ti atom to O, so that the previous electrons are globally transferred on a distance $2d$. The change of polarization associated to this transfer of charge is:

$$\delta P_\sigma = -28(\frac{V_{hd,\sigma}}{\epsilon_d - \epsilon_h})^2\delta d \tag{A10}$$

$$\delta P_\pi = -56(\frac{V_{pd,\pi}}{\epsilon_d - \epsilon_p})^2\delta d \tag{A11}$$

The associated dynamic contribution to the Born effective charge is $(\delta P/\delta d)$:

$$\delta Z_\sigma^{*(T)} = -28\left(\frac{V_{hd,\sigma}}{\epsilon_d - \epsilon_h}\right)^2 \tag{A12}$$

$$\delta Z_\pi^{*(T)} = -56\left(\frac{V_{pd,\pi}}{\epsilon_d - \epsilon_p}\right)^2 \tag{A13}$$

The effective charge on the O atom for a displacement along the Ti-O direction is therefore:

$$Z_{O\parallel}^{*(T)} = Z_O + \delta Z_\sigma^{*(T)} + \delta Z_\pi^{*(T)} \tag{A14}$$

For SrTiO$_3$, from the parameters of Matheiss (Ref. [6], p. 445), $\delta Z_\sigma^{*(T)} = -2.45$ and $\delta Z_\pi^{*(T)} = -4.76$ so that $Z_{O\parallel}^{*(T)} = -8.18$.

[†] Present address: Applied Physics Dept, Yale, P.O. Box 208284, New Haven, CT 06520-8284, USA. E-mail: philippe.ghosez@yale.edu .

[1] W. Cochran, Nature **191**, 60 (1961).
[2] R. S. Mulliken, J. Chem. Phys. **3**, 573 (1935).
[3] K. B. Wiberg and P. R. Rablen, J. Comp. Chem. **14**, 1504 (1993).
[4] J. Meister and W. H. E. Schwarz, J. Phys. Chem. **98**, 8245 (1994).
[5] M. Born and M. Goppert-Mayer, Handbuch Physik **24**, 623 (1933); M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, (University Press, Oxford, 1968), p. 265.
[6] W. A. Harrison, *Electronic structure and the properties of solids* (W. H. Freeman and Co., San Fransisco, 1980).
[7] S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987).
[8] X. Gonze, D. C. Allan, and M.P. Teter, Phys. Rev. Lett. **68**, 3603 (1992).
[9] R. D. King-Smith and D. Vanderbilt, Phys. Rev. B **47**, 1651 (1993).
[10] J. D. Axe, Phys. Rev. **157**, 429 (1967).
[11] R. Resta, M. Posternak, and A. Baldereschi, Phys. Rev. Lett. **70**, 1010 (1993).
[12] Ph. Ghosez, X. Gonze, and J.-P. Michenaud, Ferroelectrics **153**, 91 (1994).
[13] W. Zhong, R. D. King-Smith, and D. Vanderbilt, Phys. Rev. Lett. **72**, 3618 (1994).
[14] Ph. Ghosez, X. Gonze, and J.-P. Michenaud, Ferroelectrics **164**, 113 (1995).
[15] M. Posternak, R. Resta, and A. Baldereschi, Phys. Rev. B **50**, 8911 (1994).
[16] Ph. Ghosez, X. Gonze, and J.-P. Michenaud, Europhys. Lett. **33**, 713 (1996).
[17] A. W. Hewat, J. Phys. C **6**, 1074 (1973).
[18] R. A. Cowley, Phys. Rev. **134**, A981 (1964).
[19] D. Khatib, R. Migoni, G. E. Kugel, and L. Godefroy, J. Phys.: Condens. Matter **1**, 9811 (1989).
[20] A. V. Turik and A. G. Khasabov, Ferroelectrics **83**, 165 (1988).
[21] A. V. Turik and A. G. Khasabov, Ferroelectrics **164**, 345 (1995).
[22] F. M. Michel-Calendini, H. Chermette, and J. Weber, J. Phys. C **13**, 1427 (1980).
[23] R. E. Cohen and H. Krakauer, Phys. Rev. B **42**, 6416 (1990).
[24] Y.-N. Xu, W. Y. Ching, and R. H. French, Ferroelectrics **111**, 23 (1990).
[25] We note the unphysical charge on Ba. It is the result of a negative Mulliken population and reflects the inadequacy of the Mulliken population analysis which assumes an equal share of overlap between each pair of atoms.
[26] Y.-N. Xu, Hong Jiang, Xue-Fu Zhong, and W. Y. Ching, Ferroelectrics **153**, 19 (1994).
[27] W. Y. Ching and Y.-N. Xu, Phys. Rev. Lett. **65**, 895 (1990).
[28] Y.-N. Xu and W. Y. Ching, Phys. Rev. B **43**, 4461 (1991).
[29] V. V. Nemoshkalenko and A. N. Timoshevskii, Phys. Stat. Sol. (b) **127**, 163 (1985).
[30] L. T. Hudson *et al.*, Phys. Rev. B **47**, 1174 (1993).
[31] L. F. Mattheiss, Phys. Rev. B **6**, 4718 (1972).
[32] P. Pertosa and F. M. Michel-Calendini, Phys. Rev. B **17**, 2011 (1978).
[33] P. Pertosa, G. Hollinger, and F. M. Michel-Calendini, Phys. Rev. B **18**, 5177 (1978).
[34] K. H. Weyrich and R. Siems, Jap. J. Appl. Phys. **24-S2**, 206 (1985).
[35] R. E. Cohen, Nature **358**, 136 (1992).
[36] J. F. Biarge, J. Herranz, and J. Morcillo, An. R. Soc. Esp. Fis. Quim. A **57**, 81 (1961).
[37] J. Morcillo, L. J. Zamorano, and J. M. V. Heredia, Spectrochim. Acta **22**, 1969 (1966).
[38] J. Morcillo, J. F. Biarge, J. M. D. Heredia, and A. Medina, J. Mol. Struct. **3**, 77 (1969).
[39] J. Cioslowski, Phys. Rev. Lett. **62**, 1469 (1989).

[40] J. Cioslowski, J. Am. Chem. Soc. **111**, 8333 (1989).

[41] R. M. Martin and K. Kunc, Phys. Rev. B **24**, 2081 (1981).

[42] H. B. Callen, Phys. Rev. **76**, 1394 (1949).

[43] B. Szigeti, Trans. Faraday Soc. **45**, 155 (1949).

[44] E. Burstein, M. H. Brodski and G. Lucovski, Intern. J. Quantum Chem. **1S**, 759 (1967).

[45] W. Cochran, Adv. Phys. **9**, 387 (1960).

[46] Besides the different definitions of dynamical charges given in Eqs. 6, 7 and 10, let us note that another related charge is sometimes also introduced, which is defined as $Z^{*(T)}/\sqrt{\epsilon^\infty}$. This charge can reveal useful in the study of $A^N B^{8-N}$ compounds in the sense that it is directly accessible from LO-TO splitting data without any hypothesis on the amplitude of the dielectric constant. In more complex materials, as ABO_3 compounds, the extraction of the charges from the splitting is not straightforward but requires to introduce some hypothesis. This has been made by Gervais *et al.* [47] who estimated the amplitude of $Z^{*(T)}/\sqrt{\epsilon^\infty}$ in $BaTiO_3$.

[47] F. Gervais, P. Simon, P. Echegut and B. Calès, Jap. J. Appl. Phys. **24** (supplement 24-2), 117 (1985).

[48] L. D. Landau and E. M. Lifshitz, *Electrodynamics of continuous media* (Pergamon Press Ltd, Oxford, 1960), p. 42.

[49] G. Lucovsky, R. M. Martin, and E. Burstein, Phys. Rev. B **4**, 1367 (1971).

[50] G. Lucovsky and R. M. White, Phys. Rev. B **8**, 660 (1973).

[51] K. Hübner, Phys. Stat. Sol. (b) **68**, 223 (1975).

[52] W. A. Harrison, Phys. Rev. B **8**, 4487 (1973).

[53] W. A. Harrison, Phys. Rev. B **10**, 767 (1974).

[54] W. A. Harrison and S. Ciraci, Phys. Rev. B **10**, 1516 (1974).

[55] M. Lannoo and J. N. Decarpigny, Phys. Rev. B **8**, 5704 (1973).

[56] B. G. Dick and A. W. Overhauser, Phys. Rev. **112**, 90 (1958).

[57] Nominal and static charges may differ widely due to covalency effects. As the static charge is ill defined, one usually prefers to define the anomalous contribution in reference to the nominal charge. The difference between Born effective charge and static charge is sometimes referred to as the dynamical contribution.

[58] J. Bennetto and D. Vanderbilt, Phys. Rev. B **53**, 15417 (1996).

[59] D. Vanderbilt and D. King-Smith, Phys. Rev. B **48**, 4442 (1993).

[60] Ph. Ghosez and X. Gonze, submitted to Phys. Rev. B

[61] Ph. Ghosez, X. Gonze, Ph. Lambin, and J.-P. Michenaud, Phys. Rev. B **51**, 6765 (1995).

[62] W. E. Pickett, Comput. Phys. Rep. **9**, 116 (1989).

[63] M. C. Payne *et al.*, Rev. Mod. Phys. **64**, 1045 (1992).

[64] S. Goedeker, M. P. Teter and J. Hutter, Phys. Rev. B **54**, 1703 (1996).

[65] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[66] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[67] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **16**, 1748 (1977).

[68] X. Gonze, Phys. Rev. B **55**, 10337 (1997).

[69] X. Gonze and Ch. Lee, Phys. Rev. B **55**, 10355 (1997).

[70] K. M. Rabe and U. V. Waghmare, Ferroelectrics **151**, 59 (1994).

[71] R. Yu, C.-Z. Wang, and H. Krakauer, Ferroelectrics **164**, 161 (1995).

[72] C.-Z. Wang, R. Yu, and H. Krakauer, Phys. Rev. B **54**, 11161 (1996).

[73] C. Lasota, C.-Z. Wang, R. Yu, and H. Krakauer, Ferroelectrics **194**, 109 (1997).

[74] Let us mention that an early investigation of the Born effective charges of $BaTiO_3$ was performed by Last in 1957 [75], but without identifying any anomaly. Another discussion was reported in Ref. [76] but without separating the respective values of $Z^{*(T)}$.

[75] J. T. Last, Phys. Rev. **105**, 1740 (1957).

[76] T. Kurozawa, J. Phys. Soc. of Japan **16**, 1298 (1961).

[77] L. L. Boyer, H. T. Stokes and M. J. Mehl, Ferroelectrics **194**, 173 (1996).

[78] F. Detraux, Ph. Ghosez, and X. Gonze, Phys. Rev. B **56**, 983 (1997).

[79] H. Bilz, G. Benedek, and A. Bussmann-Holder, Phys. Rev. B **35**, 4840 (1987).

[80] M. Spliarsky, M. G. Stachiotti, and R. L. Migoni, Phys. Rev. B **52**, 4044 (1995).

[81] N. Marzari and D. Vanderbilt, in "Proceedings of the Fifth Williamsburg Workshop on First-Principles Calculations for Ferroelectrics", Willamsburg, VA, 1998 (available at the URL: *http://www.physics.rutgers.edu/∼dhv/preprints*); N. Marzari and D. Vanderbilt, unpublished.

[82] Depending from the structure and from the interactions, the initial position of the electron Wannier center is not necessarily on an atom. However, in the cubic perovskite structure, symmetry imposes to the Wannier centers to be located on an atom so that the anomalous contribution exactly describes the displacement from such a centered position.

[83] S. Massidda, R. Resta, M. Posternak, and A. Baldereschi, Phys. Rev. B **52**, R16977 (1995).

[84] R. E. Cohen and H. Krakauer, Ferroelectrics **136**, 65 (1992).

[85] M. Posternak, A. Baldereschi, H. Krakauer, and R. Resta Phys. Rev. B **55**, R15983 (1997).

[86] R. Resta and S. Sorella, Phys. Rev. Lett. **74**, 4738 (1995).

[87] J. C. Slater, Phys. Rev. **78**, 748 (1950).

[88] M. Posternak, A. Baldereschi, S. Massidda, and R. Resta, Bull. Am. Phys. Soc. **41**, 493 (1996).

[89] S. Öğüt and K. Rabe, Phys. Rev. B **54**, R8297 (1996).

[90] K. M. Rabe and S. Öğüt, Bull. Am. Phys. Soc. **41**, 493 (1996).

[91] Ch. Lee and X. Gonze, Phys. Rev. B **49**, 14730 (1994).

[92] Ch. Lee, Ph. Ghosez, and X. Gonze, Phys. Rev. B **50**, 13379 (1994).

[93] F. Detraux, Ph. Ghosez and X. Gonze, unpublished.

[94] L. Stixrude, R. E. Cohen, R. Yu, and H. Krakauer, American Mineralogist **81**, 1293 (1996).

[95] Ph. Ghosez, X. Gonze and J.-P. Michenaud, submitted to J. Phys.: Condens. Matter

[96] L. Bellaiche, J. Padilla and D. Vanderbilt, in "Proceedings of the Fifth Williamsburg Workshop on First-Principles Calculations for Ferroelectrics", Willamsburg, VA, 1998 (available at this URL: *http://www.physics.rutgers.edu/d̃hv/preprints*).

[97] In the tetragonal phase, shortened and elongated Ti–O bonds alternate along the ferroelectric axis. The shortened bond corresponds to an interatomic distance of 3.67 Å in our optimized tetragonal structure.

[98] C.-Z. Wang, R. Yu, and H. Krakauer, Phys. Rev. B **53**, 5430 (1996).

[99] G. Wellenhoffer *et al.*, Phys. Rev. B **53**, 6071 (1996).

[100] The Born effective charges obtained for the rhombohedral structure when neglecting the strain (i. e. when keeping a cubic unit cell) are the following: $Z^{*(T)}_{Ba,11} = +2.79$, $Z^{*(T)}_{Ba,33} = +2.79$, $Z^{*(T)}_{Ti,11} = +6.54$, $Z^{*(T)}_{Ti,33} = +5.61$, $Z^{*(T)}_{O,\perp} = -1.97$, $Z^{*(T)}_{O,\parallel} = -5.05$. These values must be compared to those reported in Table VI, where the rhombohedral strain was taken into accounts. It can be checked that the effect of this strain is negligible.

[101] H. H. Wieder, Phys. Rev. **99**, 1161 (1955).

[102] A. H. Hewat, Ferroelectrics **6**, 215 (1974).

[103] X. Gonze, Ph. Ghosez, and R. W. Godby, Phys. Rev. Lett. **74**, 4035 (1995).

[104] Ph. Ghosez, X. Gonze and J.-P. Michenaud, in "Proceedings of the VII Italian-Swiss workshop on Computational Materials Science", Cagliari, 1997.

FIG. 1. Ti-O plane cut in the partial electronic density coming from the O 2p bands in the cubic phase of barium titanate.
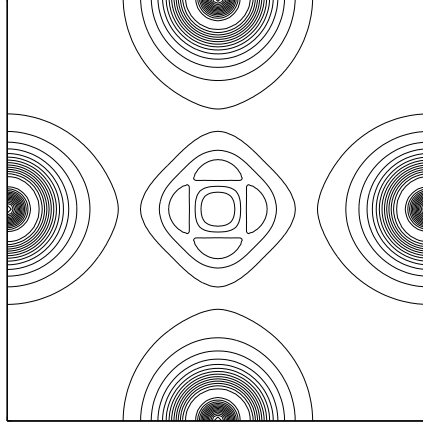

FIG. 2. Schematic representation of the two basic mechanisms that can explain the displacement of the Wannier center of a band under atomic displacement : (a) local polarizability, (b) interatomic transfers of charge.
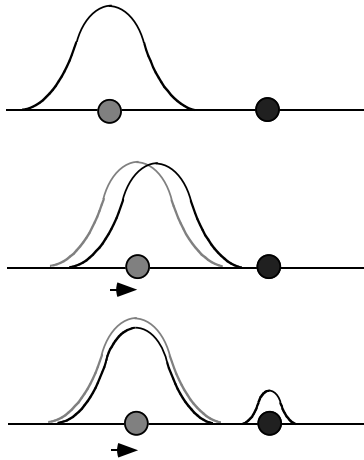
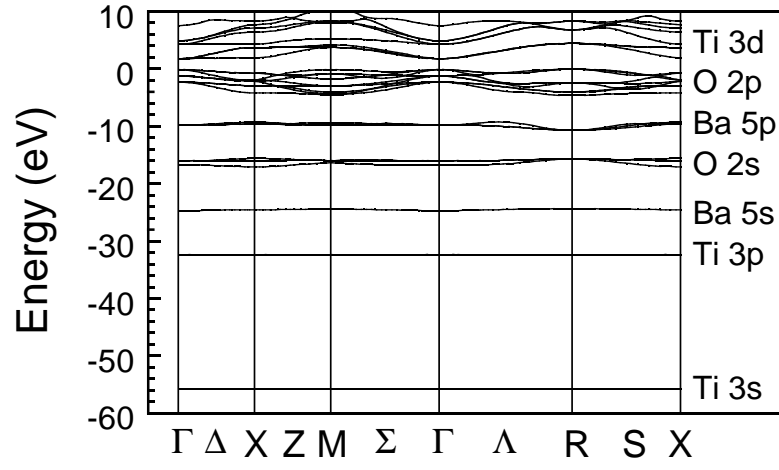FIG. 3. Kohn-Sham electronic band structure of BaTiO₃.

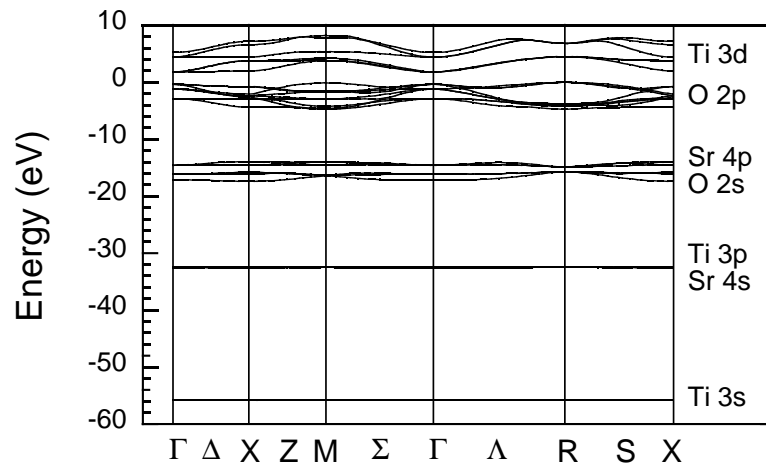FIG. 4. Kohn-Sham electronic band structure of SrTiO₃.

TABLE I. Static charges of BaTiO$_3$ in the cubic structure.

	Z_{Ba}	Z_{Ti}	Z_0	Reference
Nominal	+2	+4	−2	
Empirical models	+2.00	+0.19	−0.73	Ref. [6]
	+1.40	+2.20	−1.20	Ref. [17]
	+2.00	+1.88	−1.29	Ref. [22]
	+1.86	+3.18	−1.68	Ref. [19]
	+1.48	+1.86	−1.11	Ref. [20]
	+2.00	+1.86	−1.29	Ref. [21]
First-principles calculations	+2.00	+2.89	−1.63	Ref. [23]
	+2.12	+2.43	−1.52	Ref. [24]
	+1.39	+2.79	−1.39	Ref. [26]

TABLE II. Born effective charges of BaTiO$_3$ in the cubic structure.

		$Z_{Ba}^{*(T)}$	$Z_{Ti}^{*(T)}$	$Z_{O_\perp}^{*(T)}$	$Z_{O_\parallel}^{*(T)}$	Reference
Nominal		+2	+4	−2	−2	
Experiment		+2.9	+6.7	−2.4	−4.8	Ref. [10]
Models	(Shell model)	+1.63	+7.51	−2.71	−3.72	Ref. [61]
	(SCAD model)	+2.9	+7.3	−2.2	−5.8	Ref. [77]
First-principles	(Linear response)	+2.77	+7.25	−2.15	−5.71	Present
	(Berry phase)	+2.75	+7.16	−2.11	−5.69	Ref. [13]

TABLE III. Born effective charges of various ABO$_3$ compounds in their cubic structure.

ABO$_3$	$Z_A^{*(T)}$	$Z_B^{*(T)}$	$Z_{O_\parallel}^{*(T)}$	$Z_{O_\perp}^{*(T)}$	Reference
nominal	2	4	-2	-2	
CaTiO$_3$	2.58	7.08	-5.65	-2.00	Ref. [13]
SrTiO$_3$	2.56	7.26	-5.73	-2.15	Present
	2.54	7.12	-5.66	-2.00	Ref. [13]
	2.55	7.56	-5.92	-2.12	Ref. [73]
	2.4	7.0	-5.8	-1.8	Ref. [10]
BaZrO$_3$	2.73	6.03	-4.74	-2.01	Ref. [13]
PbTiO$_3$	3.90	7.06	-5.83	-2.56	Ref. [13]
PbZrO$_3$	3.92	5.85	-4.81	-2.48	Ref. [13]
nominal	1	5	-2	-2	
NaNbO$_3$	1.13	9.11	-7.01	-1.61	Ref. [13]
KNbO$_3$	0.82	9.13	-6.58	-1.68	Ref. [11]
	1.14	9.23	-7.01	-1.68	Ref. [13]
	1.14	9.37	-6.86	-1.65	Ref. [71]
nominal	-	6	-2	-2	
WO$_3$	-	12.51	-9.13	-1.69	Ref. [78]

TABLE IV. Band by band decomposition of $Z^{*(T)}$ in the optimized cubic phase of BaTiO$_3$. The contributions have been separated into a reference value and an anomalous charge (see text).

Band	$Z_{Ba}^{(T)}$	$Z_{Ti}^{(T)}$	$Z_{O_\perp}^{(T)}$	$Z_{O_\parallel}^{(T)}$	Total
Z_κ	$+10.00$	$+12.00$	$+6.00$	$+6.00$	$+40$
Ti 3s	$0 + 0.01$	$-2 - 0.03$	$0 + 0.00$	$0 + 0.02$	-2.00
Ti 3p	$0 + 0.02$	$-6 - 0.22$	$0 - 0.02$	$0 + 0.21$	-6.03
Ba 5s	$-2 - 0.11$	$0 + 0.05$	$0 + 0.02$	$0 + 0.01$	-2.01
O 2s	$0 + 0.73$	$0 + 0.23$	$-2 - 0.23$	$-2 - 2.51$	-6.01
Ba 5p	$-6 - 1.38$	$0 + 0.36$	$0 + 0.58$	$0 - 0.13$	-5.99
O 2p	$0 + 1.50$	$0 + 2.86$	$-6 - 0.50$	$-6 - 3.31$	-17.95
Total	$+2.77$	$+7.25$	-2.15	-5.71	$+0.01$

TABLE V. Band by band decomposition of $Z^{*(T)}$ in the experimental cubic phase of SrTiO$_3$. The contributions have been separated into a reference value and an anomalous charge (see text).

Band	$Z_{Sr}^{(T)}$	$Z_{Ti}^{(T)}$	$Z_{O_\perp}^{(T)}$	$Z_{O_\parallel}^{(T)}$	Total
Z_κ	$+10.00$	$+12.00$	$+6.00$	$+6.00$	$+40$
Ti 3s	$0 + 0.01$	$-2 - 0.03$	$0 + 0.00$	$0 + 0.03$	-1.99
Sr 4s $\}$ Ti 3p	$-2 + 0.02$	$-6 - 0.18$	$0 - 0.03$	$0 + 0.23$	-7.99
O 2s	$0 + 3.08$	$0 + 0.02$	$-2 - 1.31$	$-2 - 0.48$	-6.00
Sr 4p	$-6 - 3.11$	$0 + 0.37$	$0 + 1.42$	$0 - 0.10$	-6.00
O 2p	$0 + 0.56$	$0 + 3.08$	$-6 - 0.12$	$-6 - 3.41$	-18.01
Total	$+2.56$	$+7.26$	-2.15	-5.73	$+0.01$

TABLE VI. Born effective charges in the three ferroelectric phases of BaTiO$_3$. Tensors are reported in cartesian coordinates, with the z-axis along the ferroelectric direction. For Ba and Ti, the tensors are diagonal and only the principal elements are mentioned. For O, full tensors are reported. The eigenvalues of the symmetric part of $Z^{*(T)}$ are mentioned in brackets; the eigenvector associated to the highest eigenvalue approximately points in the Ti direction. In the cubic phase, we had: $Z_{Ti}^{*(T)} = 7.29$, $Z_{Ba}^{*(T)} = 2.74$, $Z_{O\parallel}^{*(T)} = -5.75$ and $Z_{O\perp}^{*(T)} = -2.13$.

	Tetragonal	Orthorhombic	Rhombohedral
$Z_{Ba}^{*(T)}$	(+2.72 +2.72 +2.83)	(+2.72 +2.81 +2.77)	(+2.79 +2.79 +2.74)
$Z_{Ti}^{*(T)}$	(+6.94 +6.94 +5.81)	(+6.80 +6.43 +5.59)	(+6.54 +6.54 +5.61)
$Z_{O1}^{*(T)}$	$\begin{pmatrix} -1.99 & 0 & 0 \\ 0 & -1.99 & 0 \\ 0 & 0 & -4.73 \end{pmatrix}$	$\begin{pmatrix} -2.04 & 0 & 0 \\ 0 & -3.63 & +1.38 \\ 0 & +1.57 & -3.17 \end{pmatrix}$	$\begin{pmatrix} -2.54 & -0.99 & +0.63 \\ -0.99 & -3.68 & +1.09 \\ +0.72 & +1.25 & -2.78 \end{pmatrix}$
	[−1.99 −1.99 −4.73]	[−1.91 −2.04 −4.89]	[−1.97 −1.98 −5.05]
$Z_{O2}^{*(T)}$	$\begin{pmatrix} -2.14 & 0 & 0 \\ 0 & -5.53 & 0 \\ 0 & 0 & -1.95 \end{pmatrix}$	$\begin{pmatrix} -2.04 & 0 & 0 \\ 0 & -3.63 & +1.38 \\ 0 & +1.57 & -3.17 \end{pmatrix}$	$\begin{pmatrix} -2.54 & +0.99 & +0.63 \\ +0.99 & -3.68 & -1.09 \\ +0.72 & -1.25 & -2.78 \end{pmatrix}$
	[−1.95 −2.14 −5.53]	[−1.91 −2.04 −4.89]	[−1.97 −1.98 −5.05]
$Z_{O3}^{*(T)}$	$\begin{pmatrix} -5.53 & 0 & 0 \\ 0 & -2.14 & 0 \\ 0 & 0 & -1.95 \end{pmatrix}$	$\begin{pmatrix} -5.44 & 0 & 0 \\ 0 & -1.97 & 0 \\ 0 & 0 & -2.01 \end{pmatrix}$	$\begin{pmatrix} -4.25 & 0 & -1.26 \\ 0 & -1.97 & 0 \\ -1.44 & 0 & -2.78 \end{pmatrix}$
	[−1.95 −2.14 −5.53]	[−1.97 −2.01 −5.44]	[−1.97 −1.98 −5.05]

TABLE VII. Evolution of the Born effective charges of BaTiO$_3$ under isotropic pressure in the cubic phase.

a_o (Å)	$Z_{Ba}^{*(T)}$	$Z_{Ti}^{*(T)}$	$Z_{O_\perp}^{*(T)}$	$Z_{O_\parallel}^{*(T)}$
3.67	+2.95	+7.23	−2.28	−5.61
3.94	+2.77	+7.25	−2.15	−5.71
4.00	+2.74	+7.29	−2.13	−5.75
4.40	+2.60	+7.78	−2.03	−6.31

TABLE VIII. Band by band decomposition of $Z_{Ti}^{*(T)}$ in different structure of BaTiO$_3$. The contributions have been separated into a reference value and an anomalous charge (see text).

Band	$Z_{Ti}^{*(T)}$ (cubic - 3.67 Å)	$Z_{Ti}^{*(T)}$ (cubic - 3.94 Å)	$Z_{Ti}^{*(T)}$ (tetragonal - exp)	$Z_{Ti_c}^{*(T)}$ (cubic - 4.40 Å)
Z_κ	+12.00	+12.00	+12.00	+12.00
Ti 3s	$-2 - 0.07$	$-2 - 0.03$	$-2 - 0.05$	$-2 + 0.01$
Ti 3p	$-6 - 0.43$	$-6 - 0.22$	$-6 - 0.26$	$-6 - 0.07$
Ba 5s	$0 + 0.09$	$0 + 0.05$	$0 + 0.05$	$0 + 0.02$
O 2s	$0 + 0.27$	$0 + 0.23$	$0 + 0.25$	$0 + 0.19$
Ba 5p	$0 + 0.64$	$0 + 0.36$	$0 + 0.34$	$0 + 0.13$
O 2p	$0 + 2.73$	$0 + 2.86$	$0 + 1.48$	$0 + 3.50$
Total	+7.23	+7.25	+5.81	+7.78

TABLE IX. Band by band decomposition of $Z_{Ba}^{*(T)}$ in the optimized cubic phase of BaTiO$_3$ and in an expanded cubic structure. The contributions have been separated into a reference value and an anomalous charge (see text).

Band	$Z_{Ba}^{*(T)}$ (cubic - 3.94 Å)	$Z_{Ba_c}^{*(T)}$ (cubic - 4.40 Å)
Z_κ	+10.00	+10.00
Ti 3s	$0 + 0.01$	$0 - 0.01$
Ti 3p	$0 + 0.01$	$0 + 0.01$
Ba 5s	$-2 - 0.11$	$-2 + 0.00$
O 2s	$0 + 0.73$	$0 + 0.37$
Ba 5p	$-6 - 1.38$	$-6 - 0.44$
O 2p	$0 + 1.50$	$0 + 0.66$
Total	+2.77	+2.59

TABLE X. Spontaneous polarization in the three ferroelectric phases of BaTiO$_3$ in μC/cm^2. The results were deduced from Eq. (23) when using either $Z^{*(T)}$ from the cubic phase (Cubic) or a mean charge (Mean) defined as $(Z_{mean}^{*(T)} = 0.68 \times Z_{cubic}^{*(T)} + 0.32 \times Z_{ferro}^{*(T)})$. Results are reported for the experimental (Exp) and theoretical (Theo) atomic ferroelectric displacements.

$Z^{*(T)}$	Positions	Tetragonal	Orthorhombic	Rhombohedral	Reference
$-$	$-$	26.3	30.7	33.5	Exp. [101]
Cubic	Exp	30	26	44	Ref. [13]
Cubic	Theo	36.35	42.78	43.30	Present
Mean	Theo	34.02	39.68	40.17	Present
Mean	Exp	28.64	36.11	$-$	Present